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Full paper

Interchangeable Range of Ozone Concentration Simulation for Low Cost Reconfigurable Brass Gas Cell

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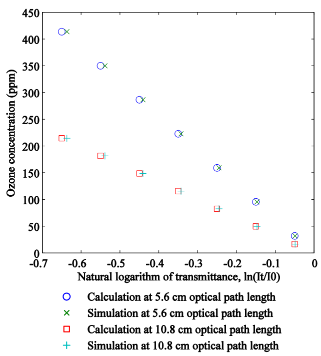
Graphical abstract



Abstract

Ultraviolet absorption spectroscopy is reliable for ozone concentration measurement. Concentration range and optical path length are inversely related based on theoretical calculation and observation of previous work. However, gas cells for ozone application are typically not expandable. In addition, they incur cost for custom fabrication. Here we design a reconfigurable brass gas cell that may interchange optical path length between 5.6 cm and 10.8 cm. Components are available at low cost, easy to joint and ready to use. Theoretical background and gas cell structure are discussed. Practical transmittance values between $e^{-0.65}$ and $e^{-0.05}$ are proposed for theoretical calculation of concentration via Beer-Lambert law. The concentration values are used in SpectralCalc.com gas cell simulation to obtain transmittance. Both approaches yield comparable result. Simulation result shows concentration range of 5.6 cm optical path length gas cell (31.82 ppm to 413.67 ppm) is wider than concentration range of 10.8 cm optical path length gas cell (16.50 ppm to 214.49 ppm). Simulation condition is at transmittance from 0.5291 to 0.9522, sampling wavelength 253.65 nm, temperature 300 K and pressure 1 atm. Thus, we strongly recommend short optical path length gas cell (5.6 cm) for wide range of concentration measurement (31.82 ppm to 413.67 ppm).

Keywords: Concentration; design; gas cell; low cost; optical path length; ozone; range; simulation

1.0 INTRODUCTION

Ozone plays an important role in our daily life because it may be viewed positively or negatively. At stratosphere, ozone filters harmful ultraviolet rays from the sun to reach the earth. Thinning of ozone layer especially in Antarctica has caused great concern among researchers [1]. At troposphere, ozone is a pollutant that affects human health and environment [2]. Therefore, much work has been done to measure ozone concentration in the sky [3, 4]. Besides, ozone is also generated on purpose for specific application. For example, ozone is used to package food [5], preserve fruit juices [6] and kill fungicides on grapes [7]. Application of ozone on food is safe because ozone is a powerful oxidizing agent that is more environmentally friendly than chlorine [8]. Ozone is naturally unstable, because it decays to oxygen. Appropriate concentration of ozone is required for food application without compromising food quality [9, 10]. Today commercial ozone analyzers are available for reliable concentration measurement. Example of this technology is absorption spectroscopy [11–20]. This is because light sensing technology is not in contact with corrosive ozone.

Concentration range and optical path length are two parameters that are closely related in absorption spectroscopy. This is because a gas cell of fixed length is observed to measure a fixed range of concentration only. Relationship between concentration range and gas cell length in previous work are summarized in Table 2. For example, concentration range is previously shown to reduce by 10 times when optical path length is increased by 10 times [12, 15]. This is supported by Beer-Lambert law in Equation 1. Concentration is inversely proportional to optical path length.

Problems occur when designing a gas cell for ozone application. Gas cell in previous work are made of aluminum [11, 13, 14], polytetrafluoroethylene (PTFE) [16] or stainless steel [20]. However, rigid gas cells are not expandable. Furthermore, the gas cells are not cost effective, because they require additional cost for custom fabrication. Here we design a low cost reconfigurable brass gas cell that has interchangeable optical path length. Optical path length change is expected to affect range of concentration measurement. Components are simple to joint and available economically.

2.0 THEORETICAL ANALYSIS

In ultraviolet absorption spectroscopy, Beer-Lambert law is a well established principle of measurement. Graph of ozone absorption cross section versus wavelength may be found in the literature [21]. Typical value of absorption cross section is large (1.147×10^{-21} m^2 molecule^{-1}) at wavelength 253.65 nm [22]. The value is previously verified to have low expanded relative uncertainty of 2.1 per cent at 95 per cent confidence level [23]. Hence, the value is considered to be accurate and used throughout current work. Good literature to explain Beer-Lambert law may be found in the literature [21, 24, 25].

$$c_{(ppm)} = -1000000RT/(\sigma N_A P l_s)\times\ln(I_t/I_0) \quad (1)$$
$$T_r = I_t/I_0 \quad (2)$$

$c_{(ppm)}$ = ozone concentration in ppm by volume
I_0 = input intensity to gas cell in count
I_t = output intensity from gas cell in count
l_s = optical path length in m
N_A = Avogadro's constant, 6.02214199×10^{23} molecule mol^{-1}
P = pressure in atm
R = ideal gas constant, 8.205746×10^{-5} atm m^3 mol^{-1} K^{-1}
T = temperature in K
T_r = transmittance
σ = absorption cross section in m^2 molecule^{-1}

Unfortunately, Beer-Lambert law (Equation 1) has limitations. For example, the law is not obeyed at low transmittance due to stray light [25]. For modern instrument, stray light is small [25]. For example, stray light of a spectrometer is less than 0.1 per cent [26]. Twyman-Lothian curve in Figure 1 is used to further explain disobedience of the law.

$$(c_{(ppm)} - c_{s(ppm)})/c_{s(ppm)}\times100 = \Delta T_r/(T_r \ln T_r)\times100 \quad (3)$$

$c_{s(ppm)}$ = known ozone concentration for standard of comparison in ppm by volume
$(c_{(ppm)} - c_{s(ppm)})/c_{s(ppm)}\times100$ = relative error of concentration (%)
ΔT_r = absolute error of transmittance

Figure 1 shows graph of relative error of concentration versus transmittance. The curve is plotted based on theoretical calculation using Twyman-Lothian equation (Equation 3) and absolute transmittance error, $\Delta T_r = 0.001$. The absolute transmittance error is equivalent to 0.1 per cent. In theory, minimum relative error of concentration (0.2718 per cent) occurs at 0.3679 transmittance. High error of relative error of concentration is observed at high transmittance [20, 24] or low transmittance [24]. Transmittance of less than 0.516 is not previously achieved for ozone concentration measurement via absorption spectroscopy [11–20]. Hence, transmittance values from $e^{-0.65}$ to $e^{-0.05}$ (0.5220 to 0.9512) are proposed because they are practical to achieve and easy to be plotted on graph.

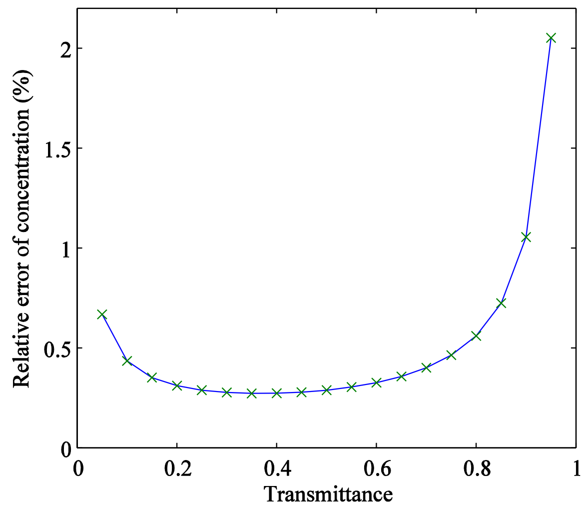


Figure 1 Twyman-Lothian curve based on absolute transmittance error 0.001

3.0 GAS CELL DESIGN

Firstly, dimensions of gas cell design will be discussed. Gas cell is designed using two identical sets of equal T brass gas connectors. Each T connector has external diameter of 0.635 cm (1/4 inch), internal diameter of 0.45 cm and length of 5.2 cm. The dimensions are ready made, as the T connector is sold as it is from local hardware shop. The dimensions are considered to be the closest to suit our application. External diameter of 0.635 cm is chosen for the gas cell to fit to silicone tube of 0.6 cm internal diameter and 0.8 cm external diameter. Internal diameter of 0.45 cm is chosen to prevent light coupling lost from 74-UV collimating lens of 0.5 cm diameter. Length of 5.2 cm is chosen to balance between response time and resolution. Response time of 5 cm gas cell (1 s) [11] is previously shown to be shorter than 63 cm gas cell (60 s) [19]. This is because gas requires long time to completely fill a long gas cell. Resolution of 5 cm gas cell (0.05 g m^{-3}, or 25.64 ppm at 300 K and 1 atm) [11] is lower than resolution of 40 cm gas cell (0.1 ppm) [18]. In other words, the longer the optical path length, the higher the ability to distinguish small concentration.

Secondly, details of connection to form a gas cell are discussed. T connectors are connected to 74-UV collimating lens from Ocean Optics. Connections between T connectors and collimating lens are fit tightly with silicone tube. The tubes also serve as inlet and outlet of ozone gas. Figure 2 and Figure 3 show two different connections to form two different gas cell. Gas cell in Figure 2 has longer optical path length (5.6 cm) compared to gas cell in Figure 3 (10.8 cm). Optical path length is calculated by summation of total gap and total length of T connector. Each lens has 0.2 cm gap between lens and edge of connection. Hence, gas cell in Figure 2 has optical path length of 0.2 cm + 5.2 cm + 0.2 cm; whereas, gas cell in Figure 3 has optical path length of 0.2 cm + 5.2 cm + 5.2 cm + 0.2 cm.

Thirdly, advantages and limitations of gas cell are discussed. Gas cell design is low cost. Equal T brass gas connector is easily available at local hardware shop at low cost of RM 6.00 each. Silicone tube is sold at RM 20 per meter. Thus, total cost is RM 32. Total cost is calculated to be RM 6 + RM 6 + RM 20. In addition, alignment and leakage of light are prevented, because brass T connectors are straight, hard and opaque. Internal diameter of gas cell stays constant at 0.45 cm. Besides, leakage of gas prevented, as silicone tube has air tight sealing property. Limitation of brass gas cell is short term usage. This is because brass is grade B (good) ozone resistant material [27, 29]. Silicone tube is grade A (excellent) ozone resistant material [27, 28, 29], but it is used to joint and seal connections. In our design, brass is major component in contact with ozone.

Equipments to be used together with gas cell are suggested. They are DH-2000 deuterium tungsten halogen source from Ocean Optics, QP400-025-SR premium solarization resistant fibers from Ocean Optics and HR4000CG-UV-NIR high resolution spectrometer from Ocean Optics. This is because deuterium halogen source emits broadband light for absorbance measurement. Solarization resistant fibers are resistant to degradation by ultraviolet light. Spectrometer reads intensity of light at specific wavelength. For example, ultraviolet intensity at 254 nm is read for measurement of ozone concentration [11].

Figure 2 Gas cell of 5.6 cm optical path length that consists of two equal T brass gas connectors that are jointed together using silicone tubes. Gas cell is connected to collimating lens, optical fibers, ozone gas inlet and outlet. Size of gas cell is compared to Malaysian 10 cent coin

Figure 3 Gas cell of 10.8 cm optical path length that consists of two equal T brass gas connectors that are jointed together using silicone tubes. Gas cell is connected to collimating lens, optical fibers, ozone gas inlet and outlet. Size of gas cell is compared to Malaysian 10 cent coin

4.0 METHODOLOGY

Firstly, calculations of ozone concentration are done using Equation 1. Details of input parameters to calculation are as follow:

Transmittance, $I_t/I_0 = e^{-0.65}, e^{-0.55}, e^{-0.45}, e^{-0.35}, e^{-0.25}, e^{-0.15}, e^{-0.05}$
$\ln(I_t/I_0) = -0.65, -0.55, -0.45, -0.35, -0.25, -0.15, -0.05$
Optical path length, $l_s = 0.056$ m, 0.108 m
Avogadro's constant, $N_A = 6.02214199\times10^{23}$ molecule mol^{-1}
Pressure, $P = 1$ atm
Ideal gas constant, $R = 8.205746\times10^{-5}$ atm m^3 mol^{-1} K^{-1}
Temperature, $T = 300$ K
Absorption cross section, $\sigma = 1.147\times10^{-21}$ m^2 molecule^{-1} [22]

Secondly, output concentration obtained from calculation is used as input to SpectralCalc.com [30] gas cell simulator as shown in Figure 4. Transmittance value at wavelength 0.25365 µm is extracted from waveband, because the wavelength is previously sampled [22] and verified to be stable [23]. Details input parameters to simulation are as follow:

Line list database = HITRAN2008
Length = 5.6 cm, 10.8 cm
Pressure = 1013.25 mbar
Temperature = 300 K
Gas = ozone (O_3)
Waveband = 0.24 µm to 0.27 µm
Isotopologue = all
Volume mixing ratio (VMR) for 5.6 cm length = 31.82×10^{-6}, 95.46×10^{-6}, 159.10×10^{-6}, 222.74×10^{-6}, 286.38×10^{-6}, 350.03×10^{-6}, 413.67×10^{-6}
Volume mixing ratio (VMR) for 10.8 cm length = 16.50×10^{-6}, 49.50×10^{-6}, 82.50×10^{-6}, 115.50×10^{-6}, 148.50×10^{-6}, 181.49×10^{-6}, 214.49×10^{-6}

Figure 4 Graphic user interface of gas cell simulator of SpectralCalc.com

5.0 RESULTS AND DISCUSSIONS

Table 1 and Figure 5 show theoretical calculation and SpectralCalc.com simulation results are in close agreement. Slight difference in transmittance value is observed. For example, gas cell of 5.6 cm optical path length is used for illustration. Transmittance values from 0.5220 to 0.9512 are input to calculation of concentration from 31.82 ppm to 413.67 ppm. However, transmittance values from 0.5291 to 0.9522 are output from simulation of the same range of concentration (31.82 ppm to 413.67 ppm). The discrepancy may be due to different absorption cross section adopted in calculation (1.147×10^{-21} m^2 molecule^{-1}) [22] and SpectralCalc.com simulation (vary between 1.123×10^{-21} m^2 molecule^{-1} and 1.124×10^{-21} m^2 molecule^{-1}). The variation exists because transmittance values are rounded up to 4 significant figures before they are applied for absorption cross section calculation via Equation 1.

Table 1 Comparison of results between theoretical calculation and SpectralCalc.com simulation

Method	Length	Concentration range	Transmittance
Calculation	5.6 cm	31.82 ppm to 413.67 ppm	0.5220 to 0.9512
Simulation	5.6 cm	31.82 ppm to 413.67 ppm	0.5291 to 0.9522
Calculation	10.8 cm	16.50 ppm to 214.49 ppm	0.5220 to 0.9512
Simulation	10.8 cm	16.50 ppm to 214.49 ppm	0.5291 to 0.9522

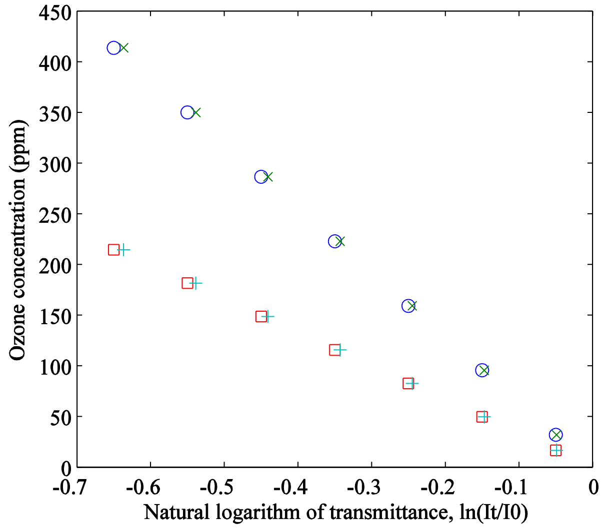


Figure 5 Graph of ozone concentration versus natural logarithm of transmittance based on theoretical calculation and SpectrcalCalc.com simulation

Figure 5 shows graph of ozone concentration versus natural logarithm of transmittance. Simulation result shows concentration range of 5.6 cm optical path length gas cell (31.82 ppm to 413.67 ppm) is almost double compared to concentration range of 10.8 cm gas cell (16.50 ppm to 214.49 ppm). The findings agree well with previous work [12, 15, 18, 19]. Explanation will be based on Table 2.

Table 2 shows comparison of concentration range between current work and previous work. Comparison should be done among previous work within similar category of light source. The shorter the optical path length, the higher the concentration range. For example, concentration range of 4 cm reflective gas cell (up to 100 ppm) [12, 15] is ten times more than concentration range of 40 cm reflective gas cell (up to 10 ppm) [12, 15]. Light emitting diode (LED) is used in these work [12, 15]. In addition, concentration range of 40 cm reflective gas cell (0.1 ppm to 10 ppm) [18] is more than concentration range of 63 cm reflective gas cell (0.05 ppm to 1 ppm) [19]. Broadband light source is used in these work [18, 19]. Hence, capability of reconfigurable gas cell to measure two distinct ranges of concentration is validated. This is because optical path length of reconfigurable gas cell is interchangeable between 5.6 cm and 10.8 cm.

Exception to this trend is observed among literature [12, 15, 17]. This is because ozone is sampled at wavelength 280 nm in previous work [17]. Typically, ozone is sampled near maximum absorption wavelength 253.65 nm [22], 254 nm [11, 18, 19] or 255 nm [12, 15] for maximum measurement sensitivity. This is the reason current work adopts sampling at wavelength 253.65 nm.

Table 2 shows concentration range of current work (31.82 ppm to 413.67 ppm) is comparable to concentration range of previous work (15.39 ppm to 497.47 ppm). This justifies the practicality to use transmittance from $e^{-0.65}$ to $e^{-0.05}$ for calculation of concentration via Equation 1. The discrepancy may be due to different optical path length applied between current work (5.6 cm) and previous work (5 cm).

Table 2 Concentration range comparison between current work simulation and previous work experiment

Optical path length	Concentration range	Light	Work
5 cm	0.03 g m^{-3} to 0.97 g m^{-3}	Broadband	[11]
5 cm	15.39 ppm to 497.47 ppm[b]		[11]
5.6 cm	31.82 ppm to 413.67 ppm[c]	Broadband	Current
4×2=8 cm[a]	tenth ppb to 100 ppm	LED	[12, 15]
10.8 cm	16.50 ppm to 214.49 ppm[c]	Broadband	Current
20 cm	0.01 ppm to 1 ppm	LED	[17]
40×2=80 cm[a]	several ppb to 10 ppm	LED	[12, 15]
40×2=80 cm[a]	0.1 ppm to 10 ppm	Broadband	[18]
63×2=126 cm[a]	0.05 ppm to 1 ppm	Broadband	[19]

[a]Length of reflective gas cell is twice of transmissive gas cell
[b]Conversion from g m^{-3} to ppm is done at 300 K and 1 atm
[c]Simulation based on transmittance from 0.5291 to 0.9522. In practice, transmittance may vary

6.0 FURTHER WORK

We suggest applying reconfigurable brass gas cell in future experimental work to measure possible ranges of concentration. Experimental result is important for verification of simulation result. Further expansion of optical path length of reconfigurable gas cell is possible by connecting more than two brass gas connectors using silicone tubes.

7.0 CONCLUSIONS AND RECOMMENDATIONS

Existing gas cells for ozone application are rigid and not expandable. In addition, fabrication cost is required to custom make the gas cells. Hence, we design a low cost reconfigurable brass gas cell for interchangeable optical path length between 5.6 cm and 10.8 cm. Components are simple to joint and bought at RM 32 altogether. Dimensions and materials used for the gas cell design are justified. Practical transmittance values between $e^{-0.65}$ and $e^{-0.05}$ are proposed to calculate concentration and plot graph. The concentrations are used to simulate transmittance via SpectralCalc.com gas cell simulator. Both approaches are found to yield similar result. Result of simulation shows concentration range of 5.6 cm optical path length gas cell (31.82 ppm to 413.67 ppm) is wider than concentration range of 10.8 cm optical path length gas cell (16.50 ppm to 214.49 ppm). Simulation is based on transmittance from 0.5291 to 0.9522, sampling wavelength 253.65 nm, temperature 300 K and pressure 1 atm. As a result, we strongly recommend short optical path length gas cell (5.6 cm) for measurement of wide range of ozone concentration (31.82 ppm to 413.67 ppm).

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